Evidence for Magnetic Field Induced Changes of the Phase of Tunneling States: Spontaneous Echoes in $(KBr)_{1-x}(KCN)_x$ in Magnetic Fields

C. Enss and S. Ludwig
Kirchhoff-Institut für Physik, Universität Heidelberg, Albert-Ueberle-Str. 3–5, 69120 Heidelberg, Germany
(Dated: February 1, 2008)

Recently, it has been discovered that in contrast to expectations the low-temperature dielectric properties of some multi-component glasses depend strongly on magnetic fields. In particular, the low-frequency dielectric susceptibility and the amplitude of coherent polarization echoes show striking non-monotonic magnetic field dependencies. The low-temperature dielectric response of these materials is governed by atomic tunneling systems. We now have investigated the coherent properties of tunneling states in a crystalline host in magnetic fields up to 230 mT. Two-pulse echo experiments have been performed on a KBr crystal containing about 7.5% CN^-. Like in glasses, but perhaps even more surprising in the case of a crystalline system, we observe a very strong magnetic field dependence of the echo amplitude. Moreover, for the first time we have direct evidence that magnetic fields change the phase of coherent tunneling systems in a well-defined way. We present the data and discuss the possible origin of this intriguing effect.

PACS numbers: 61.43.Fs, 64.90.+b, 77.22.Ch

The low-temperature properties of disordered materials like amorphous solids and crystals containing certain point defects are governed by atomic tunneling systems [1, 2]. In glasses such systems arise from the tunneling motion of single atoms or small groups of atoms between energetically almost equivalent positions separated by a potential well. In the so-called tunneling model it is assumed that these atomic tunneling systems can be approximated by particles moving in a double-well potential consisting of two adjacent harmonic wells [3, 4]. The tunneling states are characterized by two parameters, the tunnel probability $\exp(-\lambda)$ and the asymmetry energy $\varDelta$. The latter is given by the difference in depth of the two wells. As a consequence of the irregular structure of glasses, these two parameters are widely distributed. According to the tunneling model the asymmetry energy $\varDelta$ and the tunnel parameter λ are independent of each other and uniformly distributed as $P(\lambda,\varDelta)\,\mathrm{d}\lambda\,\mathrm{d}\varDelta = \overline{P}\,\mathrm{d}\lambda\,\mathrm{d}\varDelta$, providing a description of the low-temperature properties of glasses on a phenomenological basis.

In contrast to the situation in amorphous solids where the microscopic nature of the tunneling states is hitherto unknown, in crystals with certain point defects the tunneling states are well-defined and can be described on a microscopic basis [5, 6, 7]. As prominent examples we mention KCl containing Li^+, and KBr with CN^-. In a certain range of concentrations the system $(KBr)_{1-x}(KCN)_x$ is often referred to as model system for the tunneling states in glasses, because it exhibits great similarities of its low-temperature properties with those of amorphous materials [8]. The glassy properties arise from the electric and elastic interaction between the CN^- ions leading to an orientational disorder characterized by a broad distribution of the parameters of the tunneling systems like in structural glasses.

At low concentration ($x < 0.001$) the interaction between the CN^- ions can be neglected and the tunneling systems can be described in terms of isolated defects. Because of the cubic symmetry of KBr, eight potential minima in $\langle 111\rangle$ direction exist for isolated CN^- ions. For the resulting tunneling splitting $\varDelta_0/k_\mathrm{B}$ of the ground state values between 0.5 and 1.5 K have been derived from measurements of specific heat [8, 9], thermal conductivity [10] and infrared absorption [11, 12]. At intermediate concentrations ($0.01 < x < 0.1$) the presence of pairs of strongly coupled CN^- ions at next nearest neighbor sites plays an important role [13, 14, 15]. The tunnel splitting of such pairs is only of the order of 10 mK.

Until very recently it was the general belief that the dielectric properties of insulating glasses – free of magnetic impurities – are largely independent of external magnetic fields. However, new investigations have shown that the low-temperature dielectric properties of certain multi-component glasses are extremely sensitive to magnetic fields. In particular, the low-frequency dielectric susceptibility [16, 17, 18, 19, 20, 21] and the amplitude of spontaneous polarization echoes [22] show a striking non-monotonic dependence on the applied magnetic field.

To explain these findings it has been suggested that atomic tunneling systems couple directly to magnetic fields [23, 24]. In the model proposed by Kettemann *et al.* it is assumed, that some tunneling particles exist that have not just one path along which they can tunnel between the two potential minima but several — like in a Mexican hat type of potential. The presence of a magnetic field breaks the time reversal symmetry and thus changes the tunneling probability along different paths. As a result the tunnel splitting $\varDelta_0$ becomes magnetic field dependent. Since for a single tunneling system this effect is rather weak it has been suggested that the cou-

pling of a large number of such tunneling systems leads to an enhancement of the magnetic field dependence. The model by Würger considers pairs of weakly interacting two-level systems consisting of systems with roughly the same energy splitting. Such pairs have four levels, the middle two of which are almost degenerate. Due to their interaction the tunneling path of each individual tunneling system is slightly deformed, effectively turning the tunneling path of such pairs into a loop. Magnetic fields change the splitting of the almost degenerate levels noticeably and influence in this way the dielectric properties of the glass. Würger estimated that this effect would be of the right order of magnitude to explain the observed magnetic field dependence of the dielectric susceptibility in multi-component glasses.

To further investigate the influence of magnetic fields on tunneling systems, we have performed two-pulse polarization echo experiments. Since in glasses the microscopic nature of the tunneling splitting is hitherto unknown, we have decided to look for a possible magnetic field effect in crystals with tunneling defects. $(KBr)_{0.925}(KCN)_{0.075}$ was chosen because it is known to show intense polarization echoes at low temperatures due to strongly coupled pairs of CN^- ions. The sample was placed in the uniform field region of a re-entrant microwave cavity, loaded having a resonance frequency of about $\omega/(2\pi) \approx 1\,$GHz. Two short rf pulses, 100 ns and 200 ns in duration, separated by a delay time t_{12} of a few μs were used to generate spontaneous polarization echoes occurring at $2t_{12}$. The amplitude of such echoes is proportional to the number of resonant tunneling systems that stay coherent during the time interval $2t_{12}$, or in other words, have not undergone phase disturbing processes.

Fig. 1 shows the magnetic field dependence of the amplitude of two-pulse echoes generated in a single crystal $(KBr)_{0.925}(KCN)_{0.075}$ at two different electrical field strengths. As in glasses the echo amplitude is strongly influenced by external magnetic fields leading to a non-monotonic variation. Therefore, we conclude that the magnetic field dependence of the dielectric response is not a unique property of certain glasses, but also occurs in very different materials like single crystals containing point defects but no magnetic impurities. Since the origin of the tunneling states in crystals and their microscopic parameters are well-known, studies of the magnetic field effects in such materials should be very useful to gain insight into these intriguing effects.

The data shown in Fig. 1 have been obtained at two different amplitudes of the microwave pulses used to excite the echo. Clearly, at the larger electric field amplitude the magnetic effect is enhanced, indicating a non-linear electric field dependence. The overall pattern, however, appears to be unaltered. This observation agrees well with previous echo investigations of a-BaO-$Al_2O_3SiO_2$. A closer inspection of the magnetic field dependence reveals several distinct features. Close to zero field, a tiny minimum appears, that was not observed in case of a-BaO-$Al_2O_3SiO_2$. In addition, several bumps on the slope towards higher magnetic fields are present. It is tempting to assign the occurrence of these additional structures to the much narrower distribution of the tunnel splitting of CN^- pairs in $(KBr)_{0.925}(KCN)_{0.075}$ compared to the distribution in glasses. It might be that in amorphous solids the corresponding features are simply washed out.

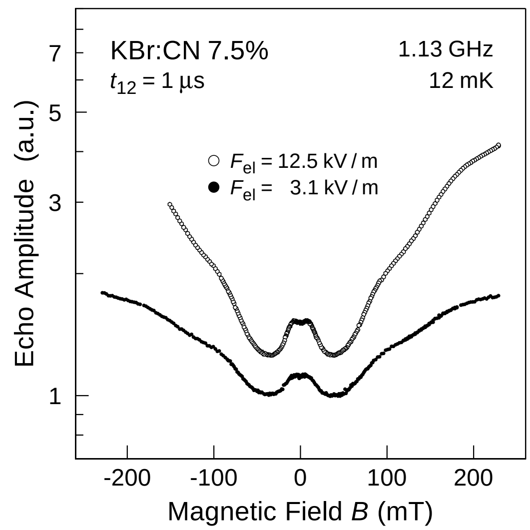

FIG. 1: Magnetic field dependence of the amplitude of two-pulse echoes generated in $(KBr)_{0.925}(KCN)_{0.075}$ excited at two different electric field strengths.

Surprisingly, the pattern changes with a variation of the delay time between the pulses. Fig. 2 shows the magnetic field dependence of the amplitude of two-pulse echoes in $(KBr)_{0.925}(KCN)_{0.075}$ obtained at different delay times. Obviously there is a systematic relation between the delay time and the magnetic field at which certain features occur. Note in particular the broadening of the central peak with decreasing delay time. This dependence indicates that the magnetic field has an influence on the phase evolution of the resonant tunneling systems, because between the two excitation pulses as well as between the second pulse and the echo the phase develops freely. To strengthen this point further we have plotted in Fig. 3 the data of Fig. 2 as a function of the product Bt_{12} of magnetic field B and delay time t_{12}. Clearly, the feature at $B \approx 0$ has now the same width for all curves and the additional structure seen at higher fields appears at roughly the same $Bt_{12} = 0.5 \times 10^{-6}\,$Ts as indicated by the two dashed lines in Fig. 3.

We conclude from this observation that the magnetic field couples to the tunneling states and changes the phase linearly with time. An obvious problem of this interpretation is that the second pulse applied in our experiment causes formally a time reversal of the phase

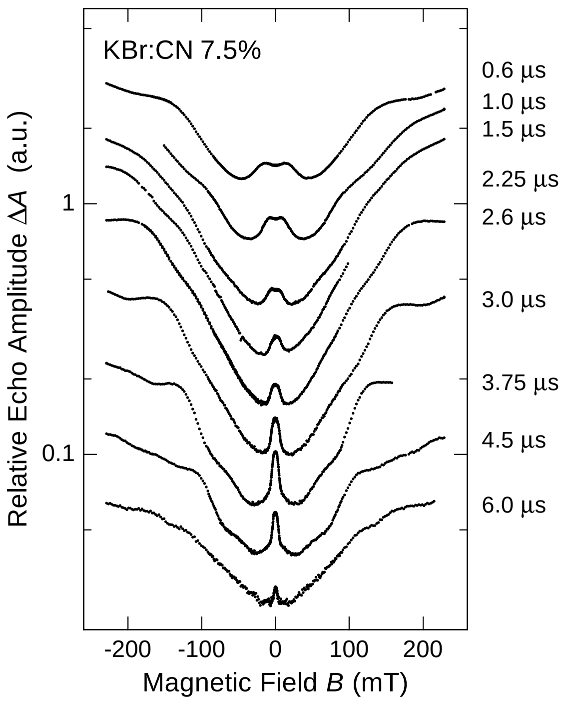

FIG. 2: Amplitude of two-pulse echoes generated in $(\mathrm{KBr})_{0.925}(\mathrm{KCN})_{0.075}$ with different delay times as a function of the applied magnetic field. The delay times are indicated on the left-hand side of this figure.

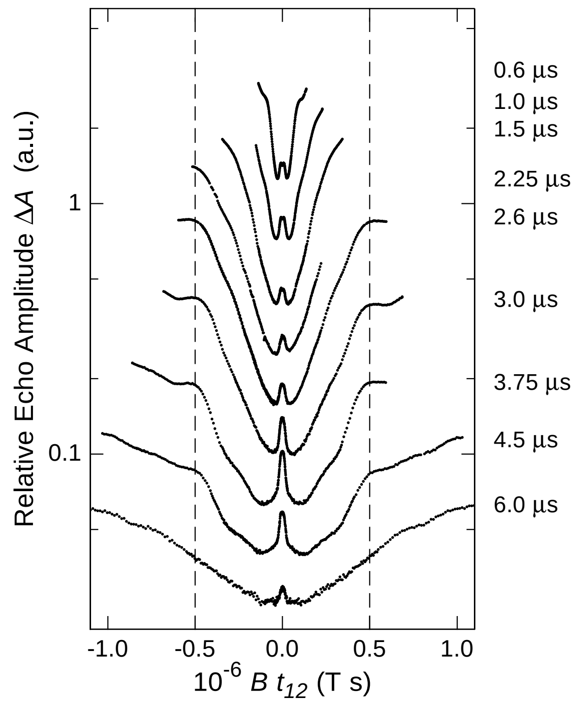

FIG. 3: Amplitude of two-pulse echoes generated in $(\mathrm{KBr})_{0.925}(\mathrm{KCN})_{0.075}$ as a function of the product of the applied magnetic field and the delay time for different delay times t_{12}. The two dashed lines mark the position of features, which appear at identical values of Bt_{12}.

development and therefore any additional phase shift accumulated during t_{12} should be compensated for in the time interval from t_{12} to $2t_{12}$. Since this is obviously not the case we have to assume that the magnetic field breaks the time reversal symmetry in this experiment.

One possible scenario that could lead to such a symmetry breaking would be a change of the magnetic moment of the tunneling systems by the microwave pulses. This is conceivable if the tunneling systems are not spherically symmetric and therefore neither the ground state nor the excited states are eigenstates of the angular momentum operator. Although isolated CN^- tunneling states in KBr crystals should exhibit a spherical symmetry, at a concentration of 7.5% the elastic interaction between the defects lead to an orientational disorder and therefore in general to a non-spherical symmetry of the tunneling systems.

It should be added that our experiments show that we are dealing with asymmetric tunneling states, because the tunnel splitting of the relevant pairs is about 10 mK [14] and the experiments have been performed at a resonance energy of 1.13 GHz corresponding to an energy of 56 mK. For such asymmetric tunneling states the effective magnetic moment will be different for each eigenstate. This means that the phase change accumulated during the time t_{12} before the inverting pulse and afterwards do not cancel exactly when the echo appears. This effect could lead to an enhanced or reduced polarization at $2t_{12}$ depending on the delay time in the experiment. Perhaps this scenario is not the only possible way in which the magnetic field breaks the time inversion symmetry in this experiment. At the present time, however, no other mechanism is known.

Let us now analyze more quantitatively the features – minima and maxima – , that coincide on the Bt_{12} plot. The width of the central peak of the curves in Fig. 3 is about 0.2×10^{-6} Ts, meaning the corresponding minimum appears at $|Bt_{12}| = 0.1 \times 10^{-6}$ Ts. The unit of this quantity is mass divided by charge. If we assume that charges comparable with an elementary charge are involved we may conclude that a mass of the order of 10 proton masses is required to account for this minimum, or equivalently, a magnetic moment of the order of a nuclear magnetic moment. The features indicated by the two dashed lines appear roughly at $|Bt_{12}| = 0.5 \times 10^{-6}$ Ts, indicating that a 5 times larger mass or in turn a 5 times smaller magnetic moment seems to be involved. At the present time this analysis is completely empirical, because we do not know whether the magnetic moments observed in our experiment are due to the orbital motion of tunneling particles or due to the nuclear magnetic moments associated with the CN^- molecule. In the latter

case it would by unclear why the nuclear magnetic moment is so strongly coupled, to the tunneling motion of the CN^- ions.

The overall increase of the echo amplitude towards larger fields does not depend on the delay time and therefore cannot be rescaled in a Bt_{12}-plot. It seems that this effect is caused by a different mechanism and is not directly related to the occurrence of the specific features mentioned above. If we again cast a glance at Fig. 1 we see that the curve obtained at higher excitation amplitude shows an increase of the echo amplitude at the largest magnetic field of 230 mT of about a factor of 3 compared to the zero field data, with the tendency of a further increase. It seems that roughly a factor of 3 more tunneling systems are moving in phase coherently at 230 mT. Since the zero field data have been obtained after adjusting the experimental parameters such that the echo amplitude had its maximum for the applied excitation pulses, the strong increase of the echo amplitude with magnetic field appears to be very mysterious.

Two possibilities for an explanation are conceivable: Either magnetic fields suppress an absorption mechanism that reduces the observed echo amplitude at zero field, or magnetic fields suppress phase perturbing processes, which dominate the dephasing a zero magnetic field. Studies of the microwave absorption in magnetic fields have shown no indication for a magnetic field dependent absorption mechanism, ruling out the first of the two possibilities. In order to investigate the second explanation, we have performed measurements of the echo decay as a function of t_{12} in different applied magnetic fields. Only a very slight influence of the magnetic field on the decay of the echo is found, which is by far not sufficient to explain the factor of three increase of the echo amplitude in magnetic fields. However, the measurement of the echo decay as a function of the delay time is only sensitive to processes which influence the free development of the phase between and after the two excitation pulses. Any phase disturbing process that would act only during the excitation pulses would not change the decay pattern as a function of delay time and therefore cannot be ruled out as a possibility. We have no plausible physical picture how such a dephasing process limited to the excitation pulses can come about, but the strong dependence of the magnetic field effect on the amplitude of the microwave field might be taken as a support for the validity of this interpretation.

In summary, magnetic field effects of the dielectric properties have been observed for the first time for a crystalline system containing point defects. A strong non-monotonic increase of the amplitude of spontaneous polarization echoes with applied magnetic field has been fund in $(KBr)_{0.925}(KCN)_{0.075}$. Certain features in the variation of the echo amplitude with the magnetic field depend on the delay time between the two exciting pulses. This observation clearly indicates that the external magnetic field couples to the tunneling systems and changes their phase relative to the external electric field in a well-defined way. The overall increase of the echo amplitude and the dependence on the electrical field strength might be explained by a hitherto unknown dephasing mechanism that only occurs during the excitation pulses.

We thank R. Weis, A. Würger, M.v. Schickfus, P. Strehlow and S. Hunklinger for helpful comments and experimental support. We are grateful to F. Luty for providing the sample. This work was supported by the Deutsche Forschungsgemeinschaft (Grant No. Hu359/11).

[1] P. Esquinazi (ed.) *Tunneling Systems in Amorphous and Crystalline Solids* (Springer, Berlin, 1998).
[2] S. Hunklinger, and C. Enss, in: Insulating and Semiconducting Glasses, ed. P. Boolchand, Series of Directions in Condensed Matter Physics **17**, 499 (World Scientific 2000).
[3] W.A. Phillips, J. Low Temp. Phys. **7**, 351 (1972).
[4] P.W. Anderson, B.I. Halperin, C.M. Varma, Phil. Mag. **25**, 1 (1972).
[5] V. Narayanamurti, R.O. Pohl: Rev. Mod. Phys. **42**, 201 (1970).
[6] F. Bridges: Crit. Rev. Solid State Sci. **5**, 1 (1975).
[7] A. Würger, *Springer Tracts in Modern Physics* (Springer, New York, 1997), Vol. 135.
[8] J.J. De Yoreo, W. Knaak, M. Meissner, R.O. Pohl, Phys. Rev. B **34**, 8828 (1986).
[9] J.N. Dobbs, M.C. Foote, A.C. Anderson, Phys. Rev. B **33**, 4178 (1986).
[10] W.D. Seward, V. Narayanamurti, Phys. Rev. **148**, 463 (1966).
[11] H.U. Beyeler, Phys. Rev. B **11**, 3078 (1975).
[12] A.L. Varma, J. Phys. C **13**, 2009 (1980).
[13] F. Luty in: *Defects in Insulating Crystals*, V.M. Turkevich, K.K. Swartz eds., Springer, 61 (1982).
[14] C. Enss, H. Schwoerer, D. Arndt, M.v. Schickfus, G. Weiss, Europhys. Lett. **26**, 289 (1994)
[15] C. Enss, H. Schwoerer, D. Arndt, M.v. Schickfus, Phys. Rev. B **51**, 811 (1995)
[16] P. Strehlow, C. Enss, S. Hunklinger, Phys. Rev. Lett. **80**, 5361 (1998)
[17] P. Strehlow, M. Wohlfahrt, A.G.M. Jansen, R. Haueisen, G. Weiss, C. Enss, S. Hunklinger, Phys. Rev. Lett. **84**, 1938 (2000).
[18] M. Wohlfahrt, P. Strehlow, C. Enss, S. Hunklinger, Europhys. Lett. **55**, (2001).
[19] R. Haueisen, G. Weiss, Proceedings of Phonon 2001, to appear in Physica B.
[20] J. Le Cochec, F. Ladieu, P. Pari, cond-mat/0203564.
[21] R. Haueisen, P. Strehlow, C. Enss, G. Weiss, to be published.
[22] S. Ludwig, C. Enss, S. Hunklinger, P. Strehlow, Phys. Rev. Lett. **88**, 075501 (2002).
[23] S. Kettemann, P. Fulde, P. Strehlow, Phys. Rev. Lett. **83**, 4325 (1999).
[24] A. Würger, Phys. Rev. Lett. **88**, 075502 (2002).